SYNTHESIS OF DIBENZYL THIOETHER USING HYDROGEN SULPHIDE AND ANION EXCHANGE RESIN AS TRI PHASE CATALYST

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Synthesis of Dibenzyl Thioether using H_2S and Anion Exchange Resin as Triphase Catalyst

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CERTIFICATE

This is to certify that the thesis entitled **"Synthesis of Dibenzyl Thioether using H_2S and Anion Exchange Resin as Triphase Catalyst"** submitted by **Kumar Vikash (108CH031)** in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology Degree in Chemical Engineering Session 2008-2012 at National Institute of Technology, Rourkela. This is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge the matter embodied in the report is his bona fide work.

Date:

Dr. Sujit Sen

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KUMAR VIKASH

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List of Abbreviations

BC	Benzyl Chloride
BM	Benzyl Mercaptan
DBS	Dibenzyl Sulphide
DEA	Diethanolamine
GLC	Gas Liquid Chromatography
MDEA	Methyl Diethanolamine
MEA	Mono Ethanolamine
PTC	Phase Transfer Catalyst
TBAB	Tetra Butyl Ammonium Bromide
TPC	Tri Phase Catalyst

Abstract

This study focuses on the utilization of Hydrogen Sulphide (H_2S) for the synthesis of Dibenzyl Sulphide (DBS) and Benzyl Mercaptan (BM). This involves first the absorption of H_2S in mono Ethanolamine and then reaction of this H_2S rich mono Ethanolamine with Benzyl Chloride for the synthesis of DBS and BM. The mono Ethanolamine and Benzyl Chloride are two different phases and their reaction is very difficult. So to carry out this reaction a phase transfer catalyst has been used. The Amberlite IR400 has been chosen as the phase transfer catalyst as it is solid and can be reused. The objective of this work is to maximize the conversion of Benzyl Chloride and maximize the selectivity of DBS. In this work the Benzyl Chloride has been used along with Toluene as a solvent. In the system under study, conversion of maximum of 90% was obtained and the desired product was obtained with 46% selectivity. Reaction time, catalyst loading, stirring speed, initial sulphide concentration and Benzyl Chloride concentration are chosen as parameters.

Keywords: Hydrogen sulphide, Dibenzyl Sulphide, Phase Transfer Catalyst, selectivity, conversion.

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CHAPTER 1

INTRODUCTION

ABSTRACT

This piece of work entails a broad overview of the present research and its vitality. It reckons an introduction to the sources of hydrogen sulphide, need to polish it off and retrieval. It also envisages upon the conventional processes used in the industries, the motto of this study and also provides an account of the organization and structure of this thesis.

1.1 SOURCES OF HYDROGEN SULPHIDE

Globally, near about 10 percent of Hydrogen Sulphide emission can be attributed to human activities. Numerous processes being carried on in the petroleum and coal industries lead to the production of gaseous by products with Hydrogen Sulphide infused into it. Hydro desulfurization is a largely accepted process in industries to make sulphur free natural gas. Petroleum refineries are one of the largest industrial pavements for Hydrogen Sulphide so far. But gradually its getting arduous to cater light and easy to process crude oil and as a consequence evident enough, refiners all over the globe are left with no other option except processing heavy crude with soaring contents of sulphur and nitrogen in it. Environmental concerns and stringent measures for the same have compelled the refiners to hydro-treat such crude to alter the sulphur and nitrogen concentrations to the set levels. Hydro treatment of heavy crude further produces enormous portions of Hydrogen Sulphide and Ammonia. Coal processing industries also involve processes responsible for the emission of Hydrogen Sulphide and Ammonia .The coal gas veritably has 0.3-3% Hydrogen Sulphide content and about 1.1% of NH_3 content as the major non-hydrocarbon adulterate. The amount of Hydrogen Sulphide of certain gas streams in natural gas industry is far too high to get commercial nod. The amount of Hydrogen Sulphide in natural gas varies between 0.1 ppm to 150,000 ppm. Coke ovens, tanneries and paper mills are the other sources of Hydrogen Sulphide arising out of the diversification of human activities.

1.2 CALL FOR TREATING HYDROGEN SULPHIDE LADEN GASES

Bit by bit but mass increase in environmental concerns has brought mounts of problems for chemical industries regarding the casting out of hazardous materials like Hydrogen Sulphide in

an acceptable way. The immense need for the removal of Hydrogen Sulphide from fluid streams is due to the reasons understated:

- Hydrogen Sulphide being a very toxic gas with 4.3%-46% explosion limits and also being heavier than air amasses at the bottom in places not having proper ventilation. It is a very dangerous gas as it sheds off its peculiar pungent smell very quickly leaving the victims unsuspecting about the impending danger of its explosion. So in order to ensure safety standards a Hydrogen Sulphide Material Datasheet (MSDS) should be consulted.
- Gas streams must be made completely free from H_2S before use and transportation owing to its odiferous, corrosive and poisonous nature. Many pipelines stipulate the extent of H2S to be below 0.25g/100 ft^3 of gas.
- The presence of H2S in the refinery gas streams can hinder the posterior processes such as equipment degradation, deactivation of catalyst, unwanted side reactions etc..

According to Occupational Health and Safety(OSHA) the permissible exposure limit for general industry is 10ppm.The American Conference of Industrial Hygienists(ACGIH) have set the threshold limit value for hydrogen sulphide as 10ppm.The national Institute for Occupational Safety and Health(NIOSH) has set the recommended exposure limit as 10 ppm. It has also set Immediately Dangerous to Life or Health concentration (IDLH) as 100 ppm.

1.3 INDUSTRIAL PROCESS FOR THE REMOVAL AND RECOVERY OF H_2S

Industries have to reduce the hydrogen sulphide emission below the safe limit in order to ensure environmental safety and health safety for their worker. Many industrial processes have been developed for the removal and the recovery of H_2S.The acidic nature of H_2S can be used for its rmoval and recovery by using alkaline solution. Strong alkaline solution like sodium hydroxide forms irreversible chemical reaction products and hence cannot be used for the removal of hydrogen sulphide from the gas streams especially if the gas contains both hydrogen sulphide and carbon dioxide where the CO_2 concentration is more than 4% (Robin,1999). So, weak alkaline solutions are used for the removal and recovery of the H_2S.

1.3.1 AMMONIA BASED PROCESS

Use of aqueous ammonia in removal of hydrogen sulphide had been well practiced (Hamblin,1973 and Harvey and Makrides,1980). The use of ammonia to remove hydrogen sulphide and carbon dioxide from gas streams has declined in recent years, but still this process is used for desulphurising coke oven gas .The basic operation in the removal of H_2S gas is :

Gas stream containing both H_2S and NH_3 is made to pass through a H_2S and a NH_3 scrubber placed in series.NH_3 scrubber is fed with stripped water from the top where ammonia is absorbed from the gas. The resulting ammoniacal solution is used as absorbent in H_2S scrubber. The solution from this unit contains ammonium sulphide, which is decomposed in deacidifier to produce hydrogen sulphide and ammoniacal liquor. The reactions occurring in this process is as shown:

$$NH_3 + H_2O \longrightarrow NH_4OH$$

$$NH_3 + H_2S \longrightarrow NH_4HS$$

$$2NH_3 + H_2S \longrightarrow (NH_4)_2S$$

Some of the advantages of ammonia based process over the ammine based process(kohl and Nielsen,1997):

- Ammonia based process is best suited for gas streams containing both H_2S and NH_3. The removal of ammonia and hydrogen sulphide is done in single step in ammonia process and in two steps in alkaolamine based process.
- When gases containing both CO_2 and H_2S are contacted with aqueous ammonia solution, the H_2S is absorbed more rapidly. The selective absorption of H_2S and CO_2 is possible in liquid ammonia by varying the concentration of liquid ammonia. By using spray column and giving short contact time, can lead to the selective absorption of hydrogen sulphide.

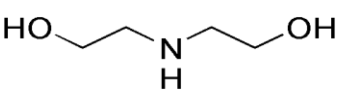
The operational difficulties associated with the ammoniacal scrubbing has restricted the use of this process as preferred method for removing hydrogen sulphide. Some of the operational difficulties associated with this process (Hamblin,1973) are:

- High partial pressure of ammonia forces the scrubbing step to be conducted with relatively dilute NH_3 solution or at relatively high pressures or a separate water wash step after the NH_3 scrubbing step in order to remove ammonia from the treated gas stream. The regeneration cost is increased with the use of dilute scrubbing solutions as it is conducted at higher temperatures.
- The regeneration of rich absorbent solution withdrawn from the scrubbing step involves the use of soluble catalysts, so sulphur product gets contaminated with the catalyst.

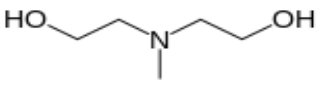
1.3.2 ALKANOLAMINE BASED PROCESS

Alkanolamine process has got wide acceptance because it has an advantage of low vapor pressure. The low vapor pressure makes the operation flexible in terms of operating- pressure, temperature and concentration.

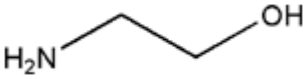
Triethanolamine(TEA),the first alkanolamine to be used in early gas treating plants (Bottoms,1930).Some of the amines that have been used are mono ethanol amine(MEA), di ethanol amine(DEA) and methyldiethanol amine(MDEA).MEA and DEA are not selective for H_2S in their reaction. The alkanol amine absorbs all acid gas components in the gas stream such as CO_2 and H_2S.



Diethanol amine(DEA)



Methyldiethanol amine



Monoethanol amine

Fig 1.1: Structural formulas of alkanolamine

Structural formulas for some of the alkanolamines are shown above. Each has atleast one hydroxyl group and one amine group. The hydroxyl group serves to reduce the vapour-pressure and increase the water solubility, while the amino group provides the necessary alkalinity in water so that the acidic gases gets absorbed.

Reaction with H_2S

$$2RNH_2 + H_2S \rightleftharpoons (RNH_3)_2S$$

$$RNH_2 + H_2S \rightleftharpoons RNH_3SH$$

Reaction with CO_2

$$2RNH_2 + CO_2 + H_2O \rightleftharpoons (RNH_3)_2CO_3$$

$$RNH_2 + CO_2 + H_2O \rightleftharpoons RNH_3CO_3H$$

$$2RNH_2 + CO_2 \rightleftharpoons RNH\text{-}CO\text{-}ONH_3R$$

The absorption reaction takes place in absorber and then stripping of absorbed gases takes place in stripping column. The concentrated H_2S gas is then subjected to sulphur recovery. The basic flow diagram of the amine-based acid gas removal process is shown in figure1.2. Treatment with alkanolamine involves the circulation of gas stream upward through the absorber, countercurrent to the stream of aqueous alkanolamine solution. The rich solution from the bottom of the absorber is heated by the heat exchanger with lean solution from the bottom of the stripping column where the absorbed gases are stripped of from the alkanol amine solution. The regenerated alkanol amine is then recycled to the absorber. The concentrated hydrogen sulphide gas obtained from top of the stripping column is then subjected to S recovery or disposal.

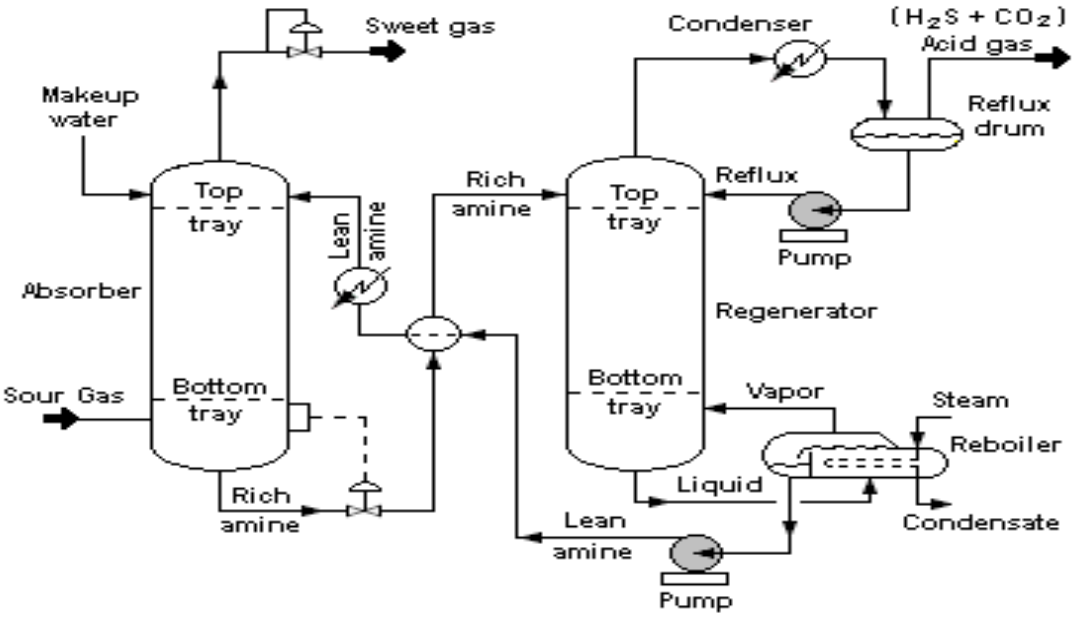


Fig 1.2: Flow Diagram of Amine Treating Process.

1.4 RECOVERY OF SULPHUR FROM HYDROGEN SULPHIDE

1.4.1 CLAUS PROCESS

Hydrogen sulphide is transformed into non- poisonous and better utility sulphur at most of the locations because of its objectionable nature. Patented after the name of the scientist Carl Friedrich Claus in 1883,this process has become an industrial benchmark. In this process, sulphur is retrieved from the gaseous hydrogen sulphide found in natural gases and other by-product gases containing hydrogen sulphide. These by-product gases originate from physical and chemical gas treatment units.

DESCRIPTION OF CLAUS PROCESS

Hydrogen Sulphide gas is put forth in the Claus unit(Fig 1.3) after being separated from the host gas using amine extraction. In this unit, the gas undergoes 2 steps:

1. Thermal Step:- The gas embedded with hydrogen sulphide reacts in a substoichiometric combustion with air in a reaction furnace at a high temperature (1000-1400^{0}C).Now the claus gases with the only combustible content "H_2S" is burnt in burner by the given chemical reaction-

$$2H_2S + 2\ O_2 \rightarrow SO_2 + 2H_2O + S$$

This includes a total flame free oxidation of H_2S generating Sulphur Di Oxide.one third of all H_2S is converted to sulphur di oxide in proper air to acid gas ratio.

2. Catalytic Step:- In this step, the reaction gases leaving the Sulphur condenser are heated again to 200-350 degree celcius and are put into a series of catalytic converter and sulphur condenser where a reaction takes place between H_2S and SO_2 to produce elemental sulphur:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

A certain amount of H_2S residue remains in the tail gas which along with other trace sulphur compounds is dealt in the tail gas unit. This can provide an appreciable sulphur recovery of about 99.8% which can further be put forth to several other uses like manufacturing medicines, cosmetics, fertilizers etc.

But, the Claus process has certain drawbacks embedded in it (Plummer, 1994 and Plummer and Beazley, 1986).Some of them are:

- It operates at high temperature
- It necessitates exact process control over oxygen and H_2S ratio.
- The tail gas released in the Claus process has very high sulphur content, unacceptable to environmental concerns and regulations.

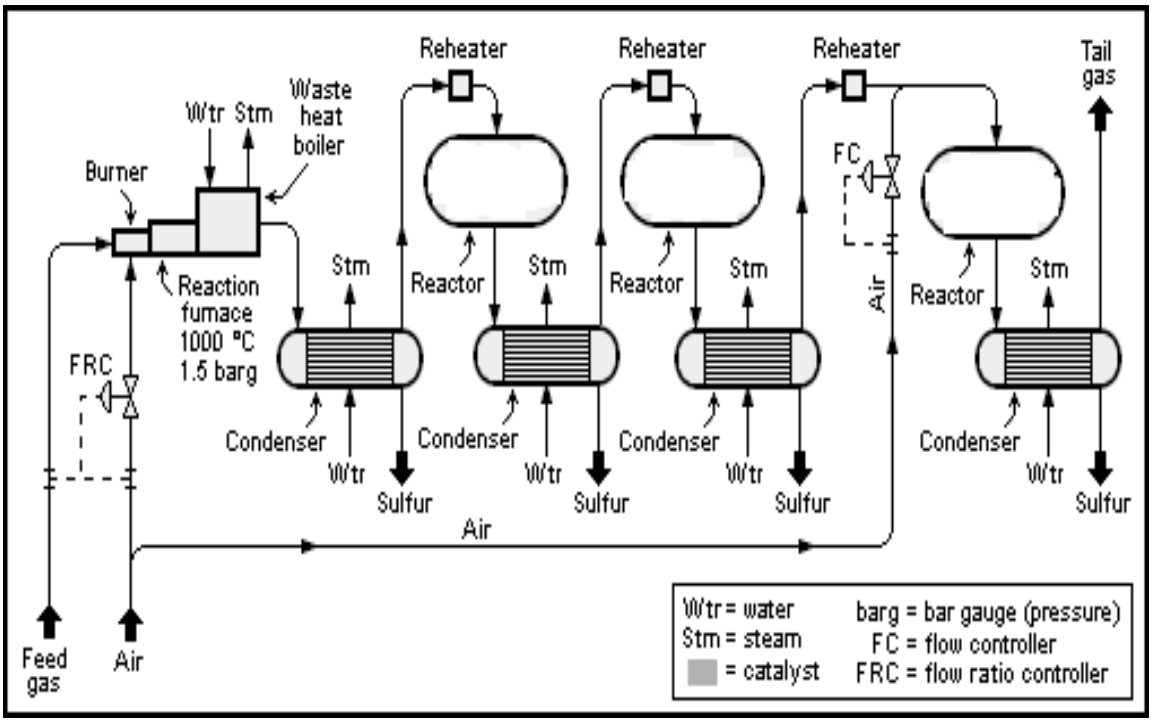


Fig 1.3: Process Flow diagram of Sulphur Recovery Unit

OTHER WAYS TO PROCESS SOUR GAS:

Amine extraction is not apt for the treatment of certain high CO_2 concentrated H_2S gases, Such streams undergo processing by the liquid redox process such as Crysta Sulf. A liquid solution containing oxidized iron is used in lieu of air in such type of processes.

As an emblem of novelty, H_2S Splitting Process is also being developed to make hydrogen as well as sulphur from H_2S.

1.4.2 CRYSTA SULF

This is a chemical process used in refineries to separate H_2S from natural gas and gas streams (Deptt. of Energy Report). In this process H_2S is converted into elemental sulphur with the help of a liquid phase claus reaction and the sulphur thus obtained is then removed by filtration. This can be a supplant to the Amine-Claus process.

Crysta Sulf process involves the spurting of heavy liquid hydrocarbon through an absorber where the liquid comes in contact with H_2S rich gas streams. In the subsequent step, H_2S gets absorbed from the gas stream and the resultant clean gas stream then leaves absorber. The H_2S prevailing in the liquid reacts with SO2 to form elemental sulphur and water.

$$2H_2S+SO_2 \rightarrow 3S+2H_2O$$

1.4.3 WET OXIDATION LO-CAT PROCESS

This process involves the conversion of H_2S into elemental sulphur with the help of an iron catalyst taking into consideration the environmental issues. The iron catalyst wrapped by organic chelated agents in a clawed pattern is introduced in a solution. The claw like fashion is aimed at not allowing the precipitation of either iron sulphide or iron hydroxide. In this process, H_2S absorbed in aqueous LO-CAT solution is oxidized to produce elemental sulphur with the reduction of iron ions from ferric to ferrous state. The reduced iron ions are transferred from the absorber to the oxidizer which is the reoxidation location of ferrous iron to ferric iron with the help of atmospheric oxygen absorbed into the LO-CAT solution thereby, regenerating the catalyst.

1.5 PRESENT WORK

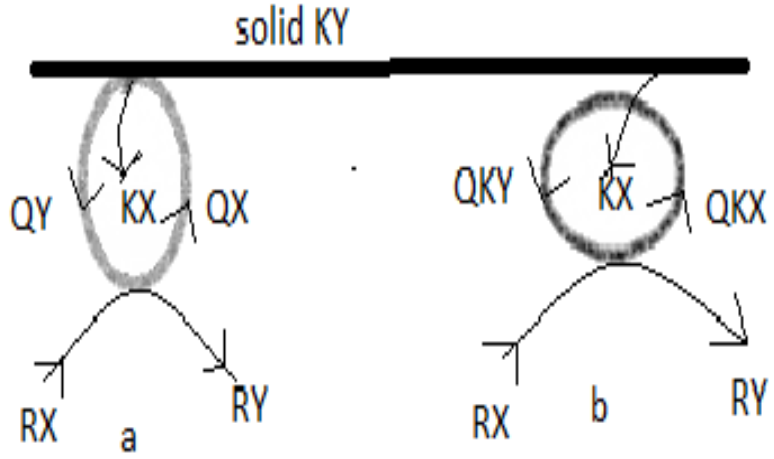
The current work is a substitute to the Claus or LO-CAT process aimed at the optimum utilization of H_2S found in various gas streams. This account deals with the process of value addition to the chemicals which utilize the H_2S found in various by-product gas streams. Keeping in view the present process, the production of value added chemicals can be attributed to H_2S rich aqueous ammonia. Present work can be dedicated to:

- Tri phase synthesis of value added fine chemicals like dibenzyl sulphide, benzyl mercaptan putting to use H_2S rich mono Ethanol amine. The entire process occurs in the presence of Amberlite IR 400 which is an effective solid Phase Transfer Catalyst(PTC).
- Emphasis upon the impact of process variables (catalyst loading, stirring speed and concentration of reactant) on the change in state of organic reactants. Reusability of catalyst is also checked. This is the main advantage of using a solid catalyst instead of a liquid catalyst.
- Formulate an apt and an operational mechanism which can optimally utilise the impacts of various parameters on the rate of reaction and conversion so that the course of reaction can be put forth in an explanatory fashion.

1.6 PHASE TRANSFER CATALYSIS

PTC is put to work basically to speed up and enhance the strength of otherwise slow heterogeneous reactions with the help of an organic layer and an ionic reactant either in liquid-liquid phase or in solid state. PTC has certain merits such as simplicity, reduced consumption of raw materials, mild operating conditions and increased rate of reaction. These special attributes provide PTC a cutting edge and priority for the purpose of organic synthesis. Quaternary Ammonium salts are the most “to be opted” class of PTC owing to their quality of action and easy availability.

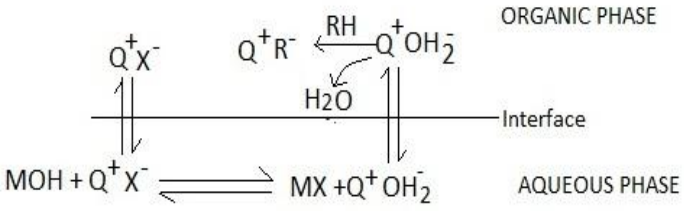
For the purpose of carrying out solid-liquid phase transfer catalysis, two mechanisms have been proposed. One among the two is suitable for conditions where the inorganic salt is substantially soluble in the given solvent and the catalyst is not able to contact the solid surface. The second mechanism is functional in situations where the inorganic salt is either insoluble or solube in negligible proportions in the organic solvent and the catalyst can approach and react with the solid surface directly. This entire mechanism is coined as homogeneous and heterogeneous solubilisation (Melville and Goddard).Increase in rate of reactions in solid-liquid phase due to small quantity of aqueous phase is termed as omega phase. Scheme 1.1 is a pictoral depiction of the 2 mechanisms:



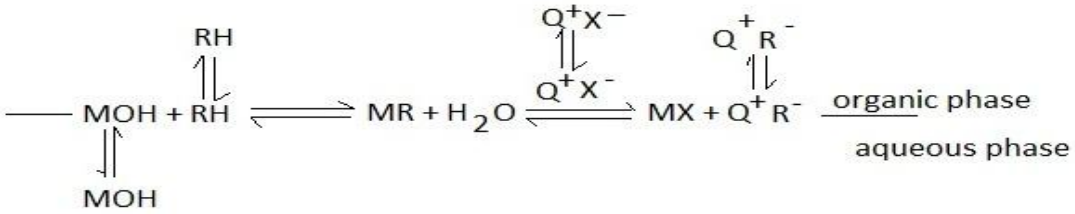
Scheme 1.1: Two distinct mechanism for Solid-Liquid Phase Transfer catalysis

a) Hetrogeneous b) Homogeneous solubilization

Interfacial and extraction mechanisms are basically used to detail the liquid-liquid phase transfer catalysis based on the lipophilicity of the quaternary cation. The extraction mechanism (scheme 1.2) propounded by starks is applied to low lipophilic catalysts such as benzyltriethylammonium and tetrabutylammoniun salts. The interfacial mechanism(scheme 1.3) allows the catalysts such as tetrahexylammonium and trioctylmethylammonium to remain in the organic phase only owing to their high lipophilicity. In this phase anions are also exchanged across the liquid-liquid interface.



Scheme 1.2: Schematic representation of Extraction mechanism.



Scheme 1.3: Schematic representation of Interfacial mechanism.

Solid phase transfer catalyst also known as Tri Phase Catalysts(TPC),offer many advantages associated with heterogeneous catalysts such as easily recovering and reusing of the catalyst and the reaction can be carried out in continuous reactor with continuously separating the catalyst.

The solid catalyst used in this work is Amberlite IRA400. It is an ion exchange resin. The polymer matrix is polystyrene DVB(polystyrene crosslinked with di vinyl benzene).The functional group is $–N^+R_3$.The ionic form is Cl^-.It appears yellow to golden yellow beads.

The aqueous phase used is mono ethanol ammine. It has got some of the advantage. They are as follows:

- The MEA has low molecular weight that results in high solution absorption at moderate concentrations (on weight basis).
- High alkalinity.
- It can be easily reclaimed from the contaminated solution.

MEA has got some of the disadvantages also.They are:

- Selective absorption of H_2S is not possible if gas stream has both CO_2 and H_2S.
- The MEA solutions are more corrosive than any other amines.
- High heat of reaction with H_2S leads to higher energy requirement for stripping.

CHAPTER 2

LITERATURE REVIEW

CHAPTER-2

LITERATURE REVIEW

Abstract

This chapter deals with the use of alkanolamine as H_2S gas absorbent, Different ways of producing Benzyl mercaptan and Dibenzyl sulphide, Use of various catalyst for the formation of valuable products using the H_2S present in gases.

2.1 USES OF ALKANOLAMINES FOR THE REMOVAL OF H_2S

As discussed in previous chapter, Kohl and Neilson,1997,showed the removal and recovery of hydrogen sulphide by the use of ammonium hydroxide. This process was developed by Hamblin,1973 which was focused on sulphur recovery. Now a days various alkanolamine are in use for the removal of hydrogen sulphide from the gas stream.Lot of research work has been done to study the solubility of hydrogen sulphide and carbon dioxide. The experimental data of solubility has been mathematically represented (Austgen et al., 1989, Lee et al., 1976, Lawson and Garst, 1976, Vallée et al., 1999, Isaacs et al., 1980, Kaewsichan et al., 2001, Al-Baghli et al., 2001, Sidi-Boumedine et al., 2004, Weiland et al., 1993).

2.2 SYNTHESIS OF BENZYL MERCAPTAN

Benzyl mercaptan is used for the manufacture of herbicides of the thiocarbamate family(Labat, 1989). It is mainly used for the synthesis of esprocarb, prosulphoarb, tiocarbazil and many more.
Hoffman and Reid (1923) prepared BM by reacting benzyl chloride with ethanolic solution of molten sodium sulfide (melted at 90^{o}C) saturated with hydrogen sulfide (H_2S). The solution was allowed to stand at low temperature,and shaking was continued for 4 days.
Heather (1988) prepared BM by reacting benzyl chloride with sodium hydrosulfide in the two-phase conditions under H_2S atmosphere at a temperature of about 50 ^{o}C until approximately 90% of the starting material was converted to the BM (stirred for approximately 5 hours), then temperature was increased by about 30 ^{o}C more for the balance of the reaction (for more 1.5 hours stirring was done).

Bittell and Speier (1978) prepared BM by using a solution of NH3 and methanol saturated with H_2S at 0^oC. Benzyl chloride was added to this methanolic ammonium hydrosulfide (NH_4SH) solution at 0^oC while slowly bubbling H_2S through the solution. It took about 1 hr for the reaction to completeh BM (92%) and DBS (8%) was produced.

Labat(1989), reacted benzyl chloride and ammonium hydrosulphide in a molar ratio of 1in a closed reactor in two steps for the preparation of benzyl mercaptan. The first step involved the addition of benzyl chloride to a hydrosulphide below 80^0C .In the second step the reaction mixture was heated at about 80^0C to 100^0C for 2hours.

2.3 SYNTHESIS OF DIBENZYL SULPHIDE

DiBenzyl Sulphide(DBS) is used an additive for extreme pressure lubricants, in refining and recovery of precious metals, in different anti corrosive formulation, anti wear additives for motor oils, stabilizers for photographic emulsions(Pradhan and Sharma, 1990).

Pradhan and Sharma(1990), produced DBS and para chlorobenzyl sulphide by reacting respective chlorides with sodium sulphide using different catalyst under liquid liquid and solid liquid mode. Out of the six catalyst they tried, TBAB(Tetra Butyl ammonium bromide) was found to be the best. In 1992 ,they also studied the reactions of nitrochlorobenzene with sodium sulphide in the presence and absence of a phase transfer catalyst and found that the solid liquid reaction is kinetically controlled in the presence of catalyst and is mass transfer controlled in the absence of catalyst.

The kinetics of reduction of nitrotoleunes by aqueous ammonium sulfide under LL PTC with the use of (TBAB) as PTC was also studied (Narayan C Pradhan, Anand V Patwardhan, Sunil K Maity, 2006). The reaction of benzyl chloride with ammonium sulfide under LL PTC using TBAB as PTC was also studied.

DBS was synthesized by reacting benzyl chloride and aqueous ammonium sulphide using TBAB as phase transfer catalyst. The parametric study was done on the selectivity of DBS. It was found that DBS can be selectively prepared by keeping high benzyl chloride concentration, High NH_3/H_2S ratio (Sujit Sen, Patwardhan, S K Maity, N C Pradhan, 2007).

The reaction of BC with H_2S rich MEA solution under L-L PTC was studied by Sujit Sen, N.C.Pradhan and Patwardhan(2010). It was found that higher ratio of MEA/H_2S favoured the formation dibenzyl sulphide and if the ratio is lower it favours the formation of benzyl mercaptan. TBAB catalyst was used.

2.4 USE OF TRI PHASE CATALYST

In the L-L PTC the catalyst was found to be soluble in both the phases and it poseses a major problem that we donot get product in pure form. For removing the dissolved catalyst it requires several water washes of the aqueous phase and treatment of the high volume of the effluent. The separation of catalyst from the reaction mixture can be achieved by extraction, distillation and adsorption and all these are energy intensive.

Pradhan and Sharma(1992),studied the catalytic effect of basic alumina and Amberlyst A27(Cl^-) form), on the reaction of benzyl chloride and para chlorobenzyl chloride with solid sodium sulphide. The catalyst used in this case is Tri Phase catalyst.

G.D Yadav and N Kirthivasan(1997) , studied the use of a novel catalyst based on heteropolyacid supported on clay, particulary dodecatungstophosphoric acid (DTP) supported on K-10 clay and they compared it with some other solid catalyst. DTP/K-10 catalyst was found to be reusable and efficient at high temperatures.

G.D Yadav and S.S Naik(2000) , prepared a clay supported phase transfer catalyst and used it for the preparation of benzoic anhydride from benzoyl chloride and sodium benzoate using clay-supported quaternary ammonium salts at 30 °C They found that clay supported catalyst were more active than polymer supported catalyst.They found the selectivity to be 100%.

G.D Yadav and A.V Joshi(2001) , used solid acid catalyst to synthesis tert amyl methyl ether (TAME) by reacting tert amyl alchohol and methanol. A comparison was made among different solid catalyst and Amberlyst-36 was found to be very effective.

G.D Yadav and O.V Badure(2007) studied the merits of creation of a third phase in biphasic reaction. They found that use of L-L-L PTC enhances the conversion and increase the selectivity also. He confirmed it by reacting phenol with benzyl chloride under L-L PTC and L-L-L PTC separately and compairing the data obtained.

S.K.Maity,Narayan C Pradhan ,Patwardhan(2008) studied reduction of p-nitrotoluene by aqueous ammonium sulphide using serelite SRA400 a triphase catalysis reaction The rate of reduction of PNT was established to be proportional to the square of the concentration of sulfide and to the cube of the concentration of PNT. Enhancement of the rate was also observed with the once used catalyst due to the presence of elemental sulphur on the surface of the catalyst.

B Gao, Z Wang, L Wang(2010) , studied the effect of different type of quaternary salt type tri phase catalyst on the esterification reaction of benzyl chloride with sodium acetate. They found that 1) Among quaternary phosphonium and quaternary ammoninum type TPC,ammonium type have the higher activity than quaternary ammonium-type catalyst, 2) TPC which is highly lipophilic, substitution takes place at N atom and they have higher catalytic activity, 3) TPC having longer spacer arm that links the quaternary onium salt group to the matrix microsphere, shows higher catalytic activity, 4) The hydrophilic and hydrophobic property of the TPC is affected by the bonding density of quaternary onium salt groupand hence influences the catalytic activity.

2.5 CONCLUSION

From literature it was found that there are two types of triphase catalyst that can be used for the synthesis of Benzyl mercaptan and Dibenzyl sulphide by reacting H_2S rich alkanolamine with benzyl chloride. They are L-L-L PTC and L-S-L PTC. The L-L-L PTC does not show very gud reusability property but they show a good conversion and selectivity. The Polymer matrix supported catalyst can have very gud reusability and selectivity is also gud. The use of solid catalyst is very useful for industrial production as the cost of catalyst is minimized by reusing it.

There is no published work on the use of Amberlite IR 400 catalyst as triphase catalyst used for reaction between H_2S rich mono ethanol amine and benzyl chloride. Amberlite IR 400 is easily available in the market as it find use in the food industries and is not much costly. The polymer matrix is divinylbenzene(gel) and it has a quartenary ammonium functional group with chloride ion attached to it.

CHAPTER 3

EXPERIMENTAL

CHAPTER 3

EXPERIMENTAL

ABSTRACT

This chapter deals with the experimental procedure followed in experimental studies.It includes chemicals, equipment details, preparation of several reagents, experimental method.

3.1 CHEMICALS

Toluene(≥99.5%) were procured from RFCL Limited, New Delhi. Amberlite IR 400 was obtained from Merck specialities Pvt. Ltd., Mumbai. Monoethanol amine (≥98%) was obtained from LOBA CHEMIE Pvt. Ltd., Mumbai. Synthesis grade benzyl chloride (≥99%) was obtained from Merck(India) Ltd., Mumbai.

3.2 EQUIPMENT

All the reactions was carried out in a mechanically agitated glass reactor of capacity 250cm^3.A 2cm diameter ,4 bladed turbine impeller was used for stirring the reaction mixture. The stirrer was kept at a height of 1.5cm (approx.) from the base of reactor and it was having the provision for speed control. The reactor was kept in a water bath so that a fixed temperature can be maintained. The schematic diagram is as shown in the figure 3.1.

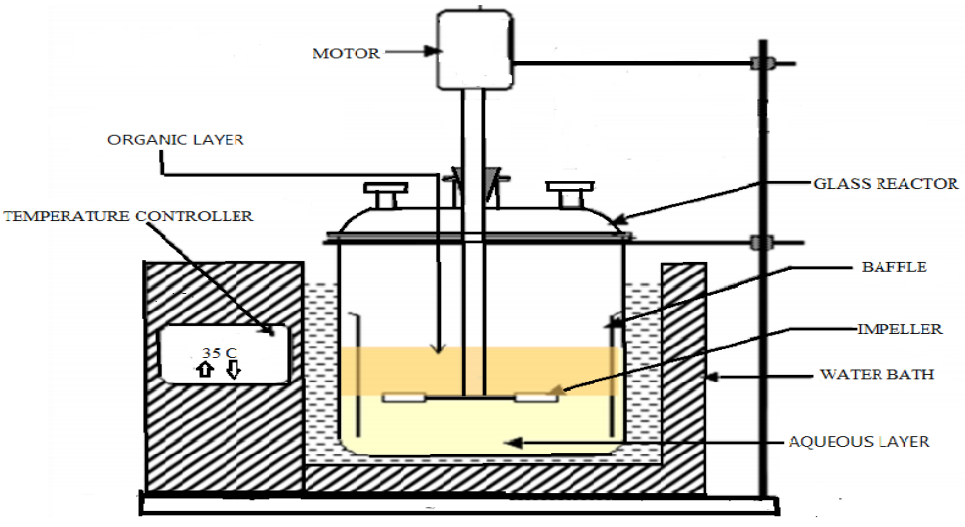


Fig 3.1: Schematic diagram of the batch reactor

3.3 PREPARATION OF H_2S RICH MONO ETHANOL AMINE

First of all, around 30-35 wt% of MEA solution was prepared by mixing appropriate amount of MEA and distilled water. Then the H_2S gas generated in the kipps apparatus was bubbled in the MEA solution in a gas bubbler. H_2S gas was prepared by reacting FeS with H_2SO_4.The concentration of H_2SO_4 was taken as 1molar.

$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$

Since the reaction between H_2S and MEA solution is exothermic (Kohl and Nielsen, 1997), the gas bubbler containing MEA solution was kept immersed in ice bath in order to prevent the oxidation of sulphide and to increase the absorbance in MEA solution as absorbance increases with decrease in temperature. The unabsorbed H_2S gas from the first bubbler was sent to second gas bubbler containing MEA solution so that the H_2S gas is vented out under prescribed environmental norms. When the gas bubbling stops, the H_2S rich MEA solution sample is withdrawn time to time and its sulphide content was analysed (Scott,1966). The gas bubbling was continued unless the desired concentration of H_2S was obtained in MEA solution. The schematic diagram is shown in fig 3.2.

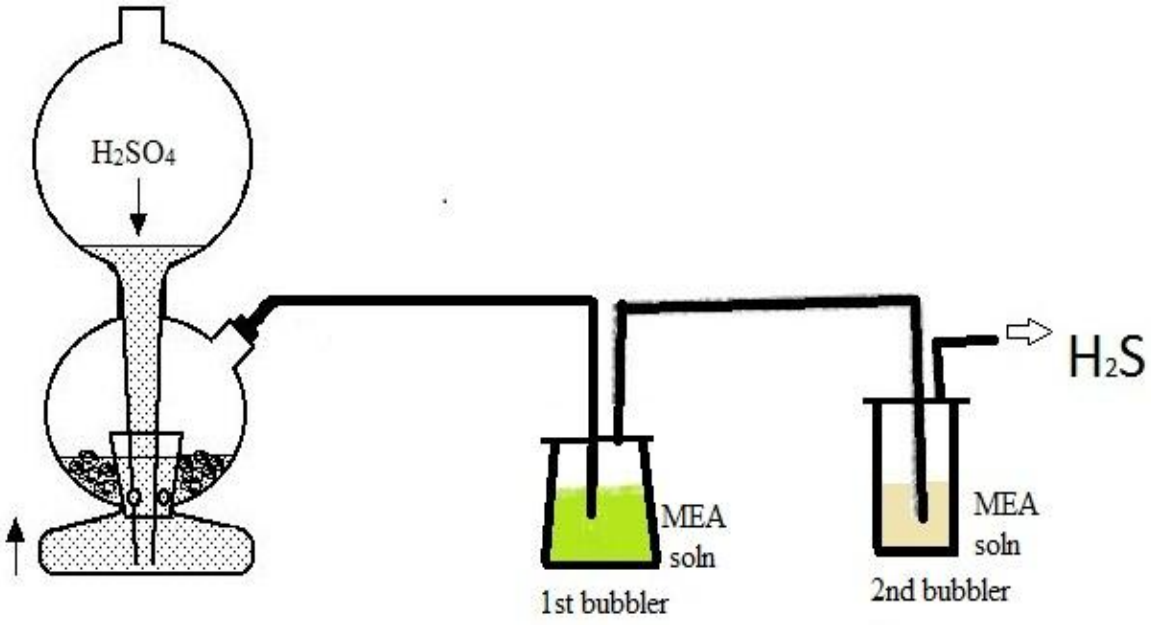


Fig 3.2: Schematic diagram for the absorption of H_2S in MEA solution

3.4 PREPARATION OF ORGANIC PHASE

Organic phase was prepared by dissolving benzyl chloride in toluene. Suppose for preparing 2.8M of organic phase we have to add 322.2ml of benzyl chloride in 677.8ml of toluene. 322.2ml of benzyl chloride corresponds to 354.42gm of benzyl chloride(density=1.1g/ml) which is equal to 2.8 moles of benzyl chloride. The total volume of solution is 1litre,and hence the strength of organic phase is 2.8M.

3.5 EXPERIMENTAL PROCEDURE

In a typical experimental run, 50cm^3 of aqueous phase containing a known concentration of sulphide is charged into the three neck batch reactor. The amount of catalyst required is weighed and fed into the reactor by the help of funnel. Then 50 ml of organic phase of known concentration of benzyl chloride was added to the reactor. The reaction mixture was then agitated at constant stirring rate. On regular time interval of 30min, 60min,120min,180min,240min,360min, 0.5ml of organic phase was taken for analysis after allowing the reaction to stop and allowing the phase separartion to occur.

3.6 ANALYSIS

3.6.1 ANALYSIS OF ORGANIC PHASE

All organic samples were analysed by the help of gas liquid chromatography(GLC) using a 2m long and 3mm in diameter stainless steel column packed with 5%SE 30. An Flame Ionisation Detector (FID) was used with nitrogen as the carrier gas. Nitrogen gas flow rate is kept at 0.8bar, injection temperature was kept at 250^{0}C and detector temperature was 300^{0}C.Oven program is set in a way that oven is maintained at 150^{0}C for 2min and then it is heated upto 300^{0}C at the rate of 20^{0}C/min and 300^{0}C is maintained for 4 min.

%Conversion = $((Ca_0 - Ca)/Ca_0) * 100\%$.

Ca_0 = Initial concentration

Ca = Final concentration

%Selectivity of DBS = (moles of DBS formed/ moles of BC converted)*100%.

3.6.2 DETERMINATION OF SULPHIDE CONTENT

Initial sulphide concentration was determined by standard iodometric titration method (Scott,1966) as given below:

Preparation of standard (0.1M) sodium thiosulphate solution:

25 gm of sodium thiosulphate pentahydrate was added in distilled water and the volume of the solution was made upto 1litre. The molecular mass of $Na_2S_2O_4.5H_2O$ is 248 gm.2-3 drops of chloroform was added to keep the solution for 1-2 days.

Standardization of $Na_2SO_4.5H_2O$ by standard KIO_3 solution:

25ml of 0.025 molar KIO_3 was taken and 1 gram excess of KI was added to it followed by adding 3ml of 1M sulphuric acid.

$$KIO_3 + 5KI + 3H_2SO_4 = 3I_2 + 3H_2O + 3K_2SO_4$$

The iodine liberated was titrated with thiosulphate solution. When the colour of solution changed to pale yellow, it was diluted to 200ml by adding distilled water .Then about 2-3 drops of 2% by weight of starch solution was added to the diluted solution.The colour of solution changed from pale yellow to blue. Then titration was continued till the colour of the solution changed from blue to colourless.

$$2\ Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

Therefore, from the above reaction it can be seen that for every 1mole of KIO_3, 6 moles of $Na_2S_2O_3$.

So,Strength of $Na_2S_2O_3$ solution = (6*strength of KIO_3*volume of KIO_3)/volume of $Na_2S_2O_3$

Preapration of 0.025M KIO_3 solution:

4.28gm of KIO_3 was weighed and added to distilled water and the volume of solution was made upto 1litre.

Estimation of sulphide concentration:

First 1ml of the concentrated sulphide solution is taken and diluted to 100 ml.15ml of standard (0.025M) KIO_3 solution is taken in a conical flask.10 ml of diluted sulphide solution was taken and added to the conical flask.10 ml of 10M NaOH solution was added to the conical flask. The mixture was gently boiled for about 10min till the colour of mixture changed from white to

colourless. Now 5ml of 5%(by wt) of KI solution and 20ml of 4M sulphuric acid solution was added to the mixture. The liberated iodine was titrated with standard sodium thiosulphate solution, which was equivalent to the unused KIO_3 solution. The potassium iodate in the alkaline medium oxidizes the sulphide to sulphate as given by the reaction:

$$4IO_3^- + 6OH^- + 3S^{2-} = 3SO_4^{2-} + 4I^- + 6H_2O$$

From the above balanced reaction we can see that 4mole of iodate ion is equivalent to3moles of sulphide ion.

So,H_2S concentration= $[15 * S_{iodate} - (V_{thiosulphate} * S_{thiosulphate})/6] * (3/4) * (100/10)$

S_{iodate} = Strength of KIO_3

$V_{thiosulphate}$ = Volume of thiosulphate

$S_{thiosulphate}$ = Strength of thiosulphate

Fig 3.3: Kipps apparatus set up in lab

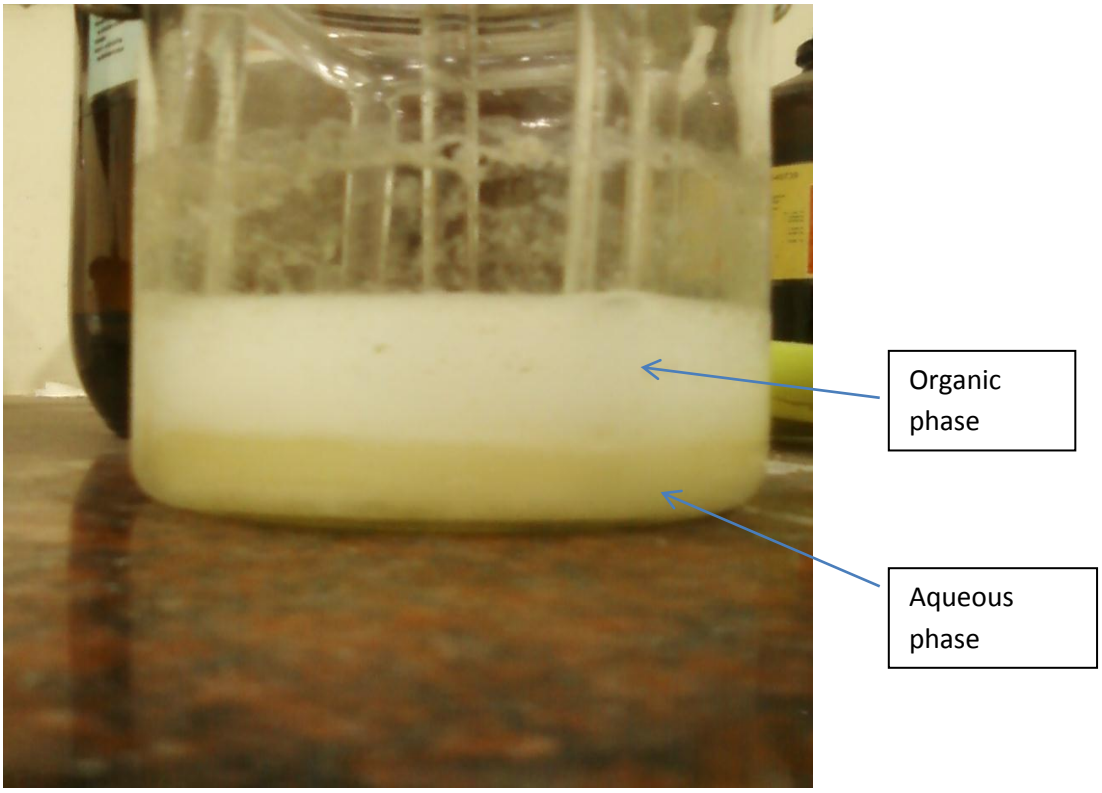


Fig 3.4: Phase separation between organic and aqueous phase

CHAPTER 4

REACTION OF BENZYL CHLORIDE WITH H_2S RICH MONO ETHANOL AMINE SOLUTION UNDER TRI PHASE TRANSFER CATALYST

CHAPTER 4

REACTION OF BENZYL CHLORIDE WITH H_2S RICH MONO ETHANOL AMINE SOLUTION UNDER TRI PHASE TRANSFER CATALYST

ABSTRACT

This chapter describe in detail the effect of various parameters on the synthesis of di benzyl sulphide and benzyl mercaptan from the reaction of H_2S rich mono ethanol amine and benzyl chloride in the presence of Amberlite IR 400 a triphase catalyst.The parameters studied are catalyst loading, stirring speed and reusability of the catalyst is checked.

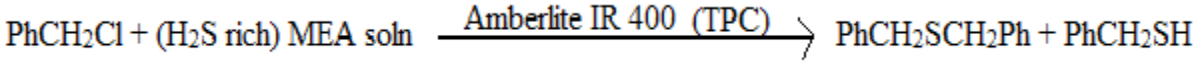
4.1 INTRODUCTION

In refineries, H_2S gas is removed from various gas streams by dissolving in alkanol amine solution. The alkanol amine is regenerated in stripper and the H_2S gas so obtained is used for producing elemental sulphur by using clauss process.This process consumes lot of energy in stripping and various other steps. So if this H_2S rich amine can be used for producing different valuable chemicals, then it would of great value in refineries as H_2S is produced in large scale here.

High alkalinity of mono ethanol amine can be used for absorbing hydrogen sulphide gas. The reaction between benzyl chloride and H_2S rich mono ethanol amine gives benzyl mercaptan and dibenzyl sulphide which is of great industrial value and is a more valuable product than elemental sulphur. Dibenzyl sulphide is used as an additive for extreme pressure lubricants , anti-wear additive for motor oil, stabilizer for photographic emulsion, in refinery and recovery of precious metal and in different anti corrosive formulation. Benzyl mercaptan is having medicinal value and is used for the formation of herbicides.

The benzyl chloride and MEA are having different densities and hence, are of two different phase. Hence, for better reaction and for formation of desired product it required the use of a catalyst. From literature it has been found that a lot of liquid catalyst have been used for the reaction of benzyl chloride and H_2S rich MEA solution such as TBAB(Tetra Butyl Ammonium Bromide), PEG (Poly ethaline glycol), etc. The problem with these liquid catalyst is that they cant be separated easily from the solution after adding and hence purity of the product is not so

good. This also creates a problem as quaternary ammonium compounds are harmful in liquid effluents. Liquid catalyst is lost after its use so cost of catalyst increases the cost of production. So considering the cost and purity of product solid catalyst has to be used. Amberlite is used as it is not much costly and is easily available. The overall reaction can be represented by scheme 4.1:



Scheme: 4.1

Parametric studies have been performed following one variable at a time approach to see the effect of various parameters such as stirring speed, catalyst loading on benzyl chloride conversion and DBS selectivity. The reusability of the catalyst was also checked.

4.2 RESULTS AND DISCUSSION

4.2.1 PARAMETRIC STUDY

4.2.1.1 EFFECT OF STIRRING SPEED

Elimination of mass transfer resistance is very important in order to do kinetic study. The effect of stirring speed was studied under the range of 1000-2000 rpm, other conditions were kept identical in the presence of Amberlite IR 400 catalyst. The data obtained is shown in figure 4.1. From the figure it was observed that under this range of stirring speed, the variation in benzyl chloride conversion was very small. This indicates that the mass transfer factor is very negligible and hence other reactions were carried out at a stirring speed of 1500 rpm to ensure the absence of mass transfer resistance.

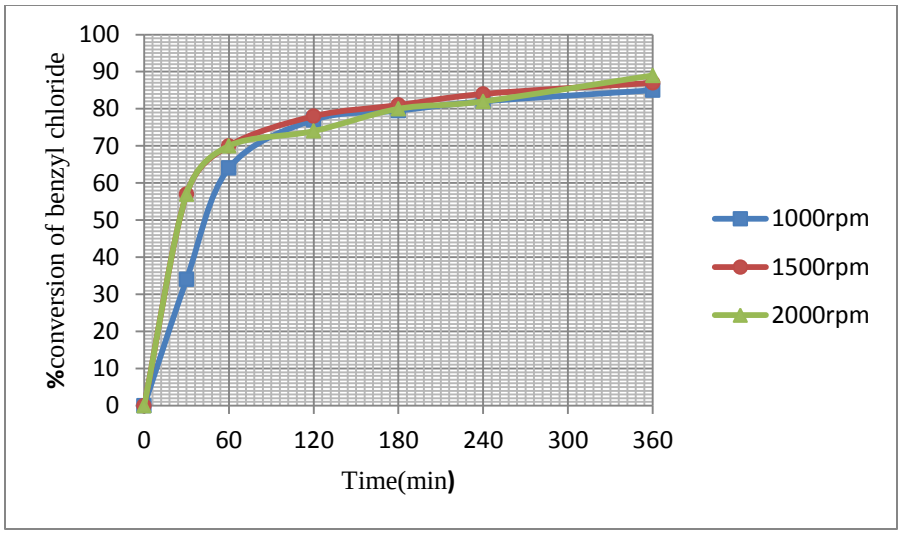


Fig 4.1: Effect of Stirring Speed on the conversion of BC.

Operating Conditions:

Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of benzyl chloride – 2.8M, Sulphide concentration – 2.3M, MEA/H_2S ratio – 2.1, Temperature - 35^0C, Catalyst loading – 10%(w/v).

4.2.1.2 EFFECT OF CATALYST LOADING

The effect of catalyst Amberlite IR 400 loading was studied in the range of 0%(w/v) to 15%(w/v). The data obtained is shown in figure 4.2(a). With the increase of catalyst loading the benzyl chloride conversion increases. From the graph it can be seen that with the increase of catalyst loading the conversion increased from 64% without catalyst to more than 70 % after 6 hours of operation. It can be also observed from the figure 4.2(a), that after 10%(w/v) catalyst loading , the conversion is almost same.This shows that the mass transfer of the active species reaches to a maximum value after 10%(w/v) catalyst loading.

The selectivity of Dibenzyl sulphide increases with the increase in catalyst loading. This is shown in figure 4.2(b). DBS and BM is formed due to the transfer of QSQ and QHS to the organic phase. QSQ and QSH are formed by the reaction of Q^+ ion obtained from the catalyst with the HS^- and S^{2-} present in the aqueous phase. This QSQ and QSH reacts with the benzyl chloride and neucleophilic substitution takes place and DBS and BM is formed. So more catalyst concentration, more Q^+ ion will be present and hence more QSQ will be formed, which will

result in the formation of more DBS. Therefore, the selectivity of DBS increases with the increase in catalyst loading.

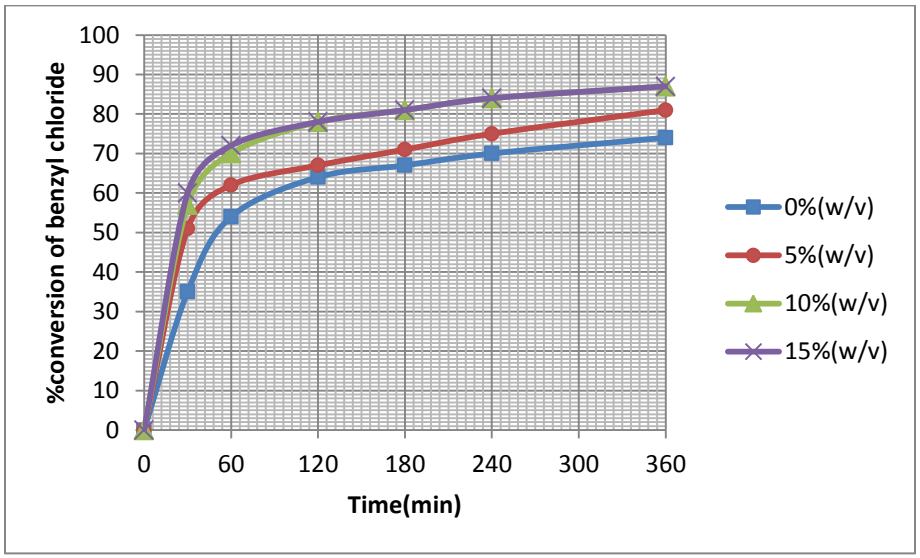


Fig 4.2(a): Effect of catalyst loading on the conversion of BC.

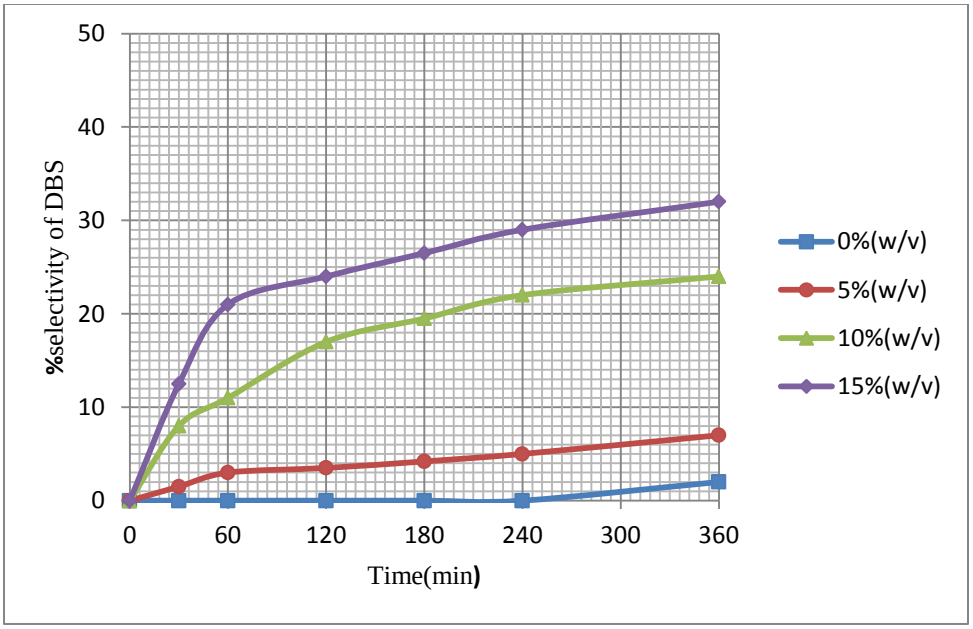


Fig 4.2(b): Effect of catalyst loading on the DBS selectivity.

Operating Condition :

Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of benzyl chloride – 2.8M, Sulphide concentration – 2.3M, MEA/H_2S ratio – 2.1, Temperature - 32^0C, Stirring speed – 1500 rpm.

4.2.1.3 EFFECT OF INITIAL SULPHIDE CONCETRATION

For a fixed MEA concentration of 3.5M, the effect of variation of initial sulphide content was studied. With the increase of initial sulphide content, the conversion increases because of the presence of more amount of sulphide ions. The data obtained is shown in figure 4.3(a).But for the case of selectivity, the selectivity of DBS decrease with an increase in the initial sulphide concentration. For fixed amount of MEA, the increase in the sulphide concentration decreases the MEA/sulphide mole ratio in the aqueous phase.This is responsible for determining the concentration of sulphide ion and hydrosulphide ion in MEA. In the presence of more MEA or it can be said that in presence of high MEA/ sulphide molal ratio, the dissociation equilibrium shifts towards more ionization and hence more sulphide ions(S^{2-}) are formed compared to hydrosulphide(HS^{-}) ion. The data is shown in figure4.3(b).

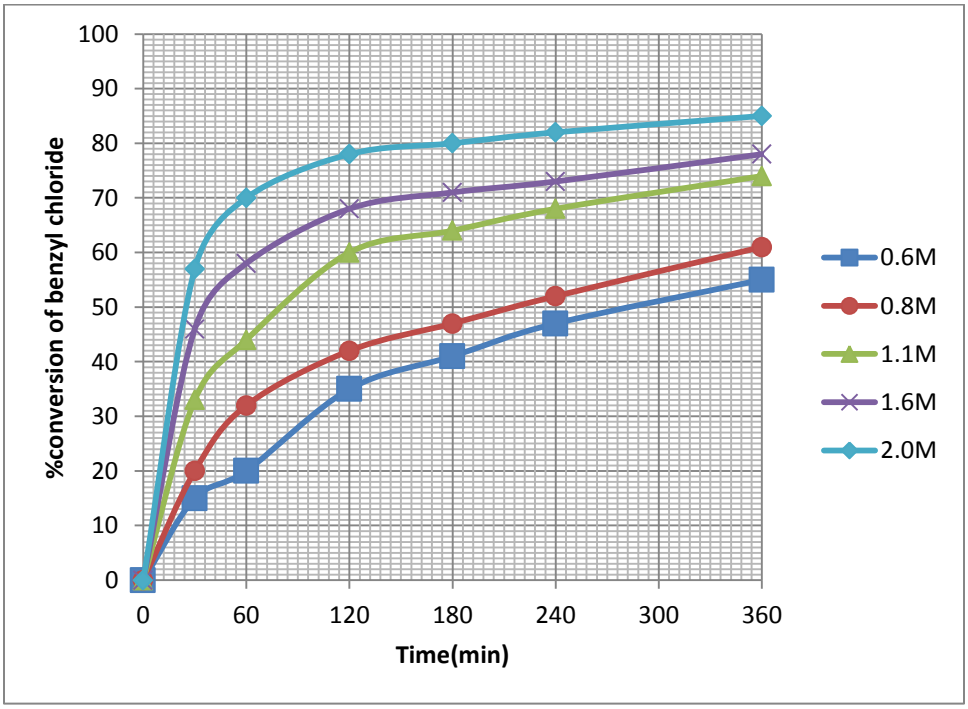


Fig 4.3(a): Effect of initial sulphide concentration on the conversion of BC.

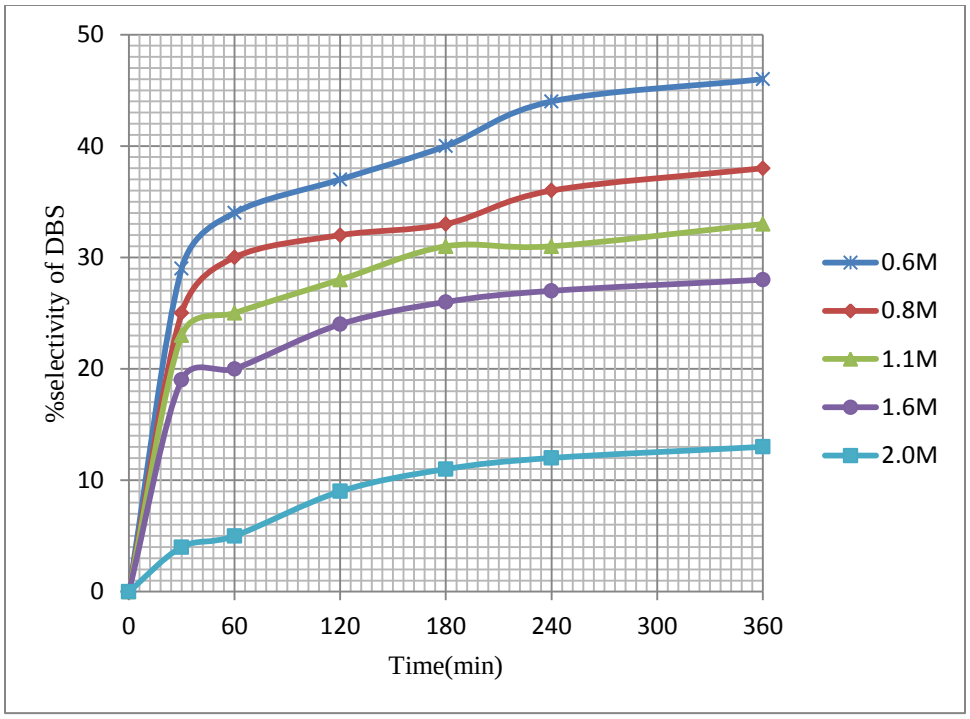


Fig 4.3(b): Effect of initial sulphide concentration on DBS selectivity.

Operating Condition :

Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of benzyl chloride – 2.8M, MEA concentration – 3.5M, Temperature - 31^0C, Stirring speed – 1500 rpm. Catalyst loading – 10%(w/v).

4.2.1.4 EFFECT OF BENZYL CHLORIDE CONCENTRATION

The benzyl chloride concentration effect was studied on benzyl chloride conversion and DBS selectivity. As seen from the figure 4.4(a), we find that with the increase of benzyl chloride concentration the conversion of benzyl chloride decreases. This is because sulphide content is same for all cases but the benzyl chloride concentration increases that reduces the conversion.

But for the case of selectivity, the selectivity of DBS increases with the increase in the concentration of benzyl chloride. This is because at low benzyl chloride concentration there is insufficient amount of benzyl chloride to produce DBS which result in low selectivity. The data is represented in fig 4.4(b).

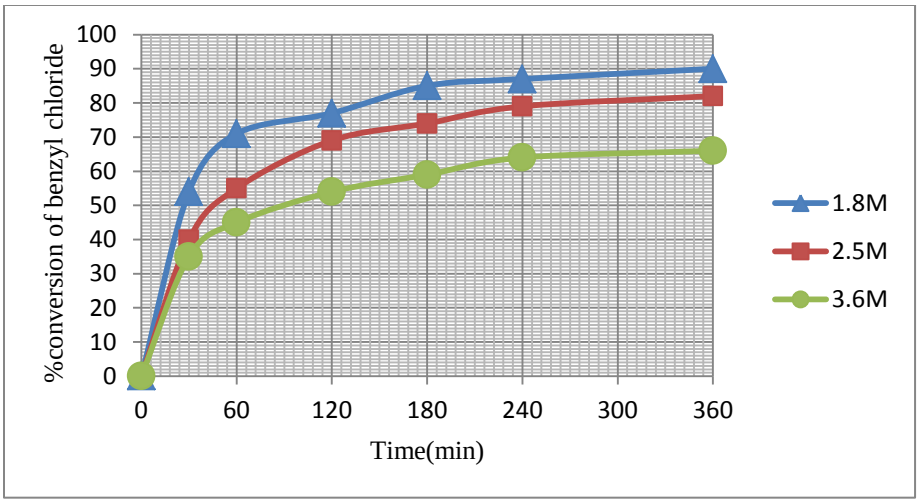


Fig 4.4(a): Effect of BC concentration on the conversion of BC.

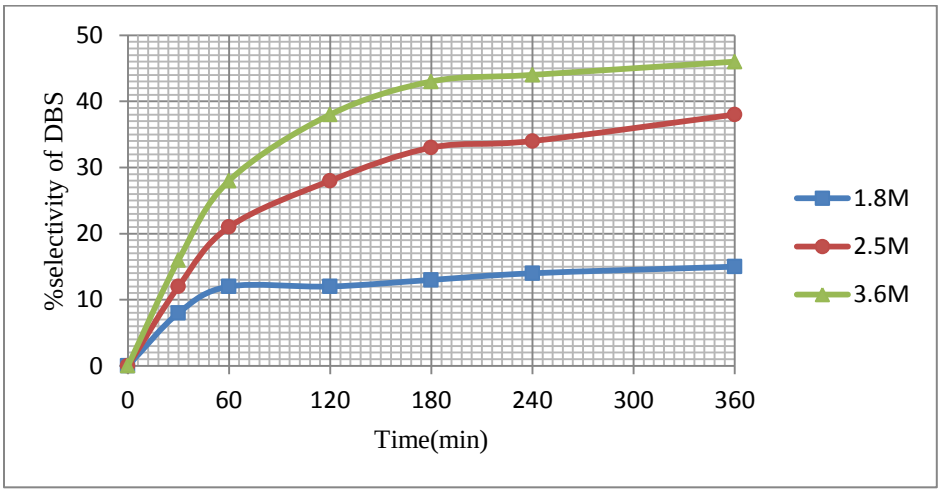


Fig 4.4(b): Effect of BC concentration on DBS selectivity.

Operating Condition :

Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Sulphide concentration – 1.12M, MEA/H_2S ratio – 3.18, Temperature - 33^0C, Stirring speed – 1500 rpm, Catalyst loading – 10%(w/v).

4.2.2 RECYCLE AND REUSE OF AMBERLITE IR400

After the use the catalyst microsphere was filtered from the solution by the use of filter paper. It was washed with acetone and water and was dried to remove the adsorbed substance. The catalyst obtained was reused and the data obtained is shown in figure 4.5.

Figure 4.5 shows the conversion of benzyl chloride with the cycle number. It can be seen that after 4 cycles, the activity of tri phase catalyst Amberlite remains nearly unchanged. This tells that amberlite has got excellent reuse property and high stability.

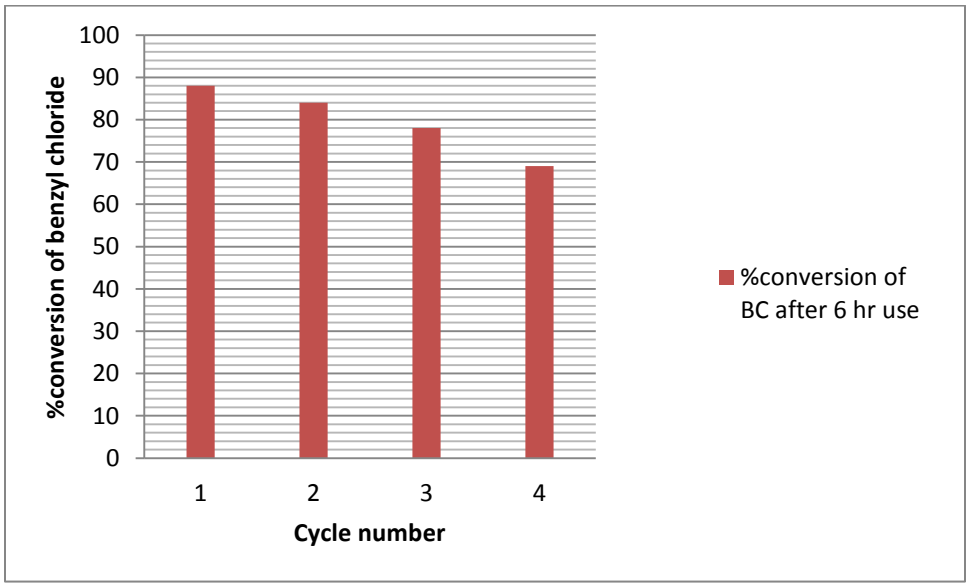


Fig 4.5: Effect of cycle number of reuse on the catalytic activity.

Operating Condition :

Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of benzyl chloride – 2.8M, Sulphide concentration – 2.3M, MEA/H_2S ratio – 2.1, Temperature - 33^0C, catalyst loading = 10%(w/v), Stirring speed – 1500 rpm.

4.2.3 REACTION MECHANISM

The reaction mechanism depends on the lipophilicity of the catalyst. If the catalyst is highly lipophilic it means that it can dissolve in both the phases that is in aqueous and organic phases and hence they will follow interfacial mechanism. But if the catalyst is not lipophilic then it will not dissolve in both the phases and hence they will follow extraction mechanism. The AmberliteIR 400 is a solid catalyst and is not soluble in any phase so it will follow extraction mechanism. However, it was observed that the gel beads swells. The beads remain in organic phase and ammonium ion remains in aqueous phase. Since the neucleophilicity of sulphide ion and hydrosulphide ion is more than that of the chloride ion present in the catalyst, it replaces chloride ion on the catalyst. The following reaction takes place:

In aqueous phase catalyst swells and the negative chloride ion on the catalyst is exchanged by HS^- and S^{2-} ion of the aqueous phase. The following reaction takes place:

Aqueous Phase:

$$RNH_2 + H_2S \longrightarrow RNH_3^+ + HS^-$$

$$RNH_2 + HS^- \longrightarrow RNH_3^+ + S^{2-}$$

$$HCl + RNH_2 \longrightarrow RNH_3^+ + Cl^-$$

Reaction at interface:

$$Q^+Cl^- + HS^- \longrightarrow QSH + Cl^-$$

$$2Q^+Cl^- + S^{2-} \longrightarrow QSQ + 2Cl^-$$

The polymeric microsphere bearing the active ion pairs when it reaches the bulk organic phase then it release nucleophilic species:

$$QSH \longrightarrow Q^+ + HS^-$$

$$QSQ \longrightarrow Q^+ + QS^-$$

$$QS^- \longrightarrow Q^+ + S^{2-}$$

Due to the reaction of benzyl chloride with HS^- and S^{2-} produces DBS and BM.

$$C_6H_5CH_2Cl + HS^- \longrightarrow C_6H_5CH_2SH + Cl^-$$

$$C_6H_5CH_2Cl + S^{2-} \longrightarrow C_6H_5CH_2SCH_2C_6H_5 + Cl^-$$

The released chloride ion combines with Q^+ and the catalyst is regenerated.

From the concentration profile of a typical run Figure 4.6,it is seen that the concentration of benzyl mercaptan rises to a maximum and decreases whereas the concentration of DBS keeps on continuously increasing. From this we can conclude that the benzyl mercaptan combines with benzyl chloride to produce dibenzyl sulphide and HCl.

$$C_6H_5CH_2Cl + C_6H_5CH_2SH \longrightarrow C_6H_5CH_2SCH_2C_6H_5 + HCl$$

Since BM is the weak acid so this reaction is slow. This HCl generated reacts with MEA to form methanol amine hydrochloride.

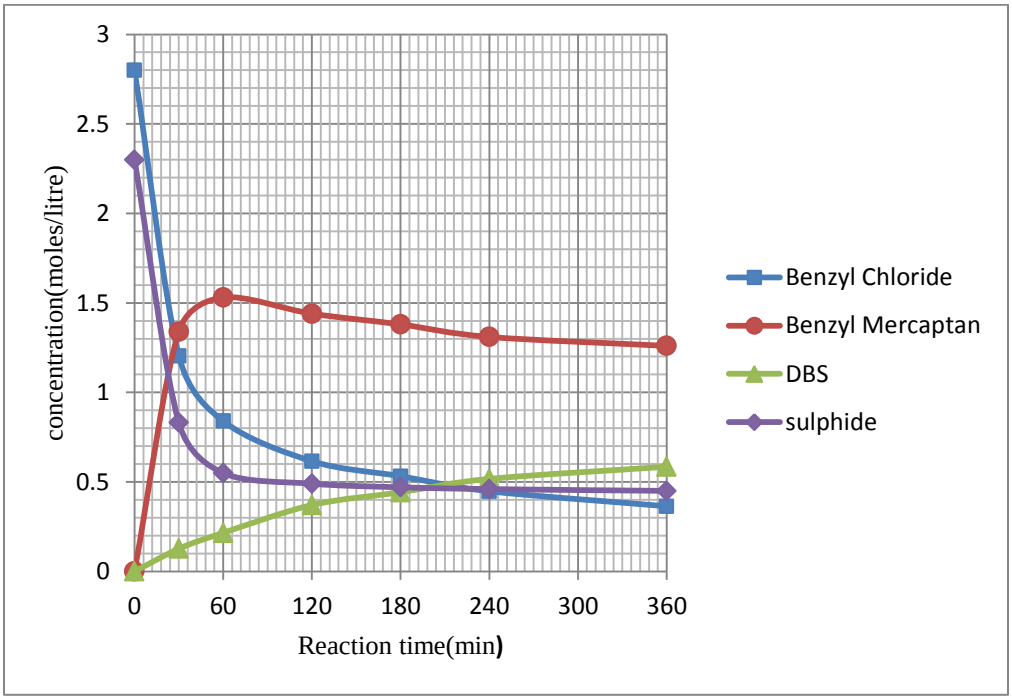


Fig 4.6: Concentration profile for a typical run.

Operating Condition :

Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of benzyl chloride – 2.8M, Sulphide concentration – 2.3M, MEA/H_2S ratio – 2.1, Catalyst loading – 10%(w/v), Temperature - 32^0C, Stirring speed – 1500 rpm.

4.3 CONCLUSION

The reaction between H_2S rich MEA and benzyl chloride in the presence of amberlite IR400 which is a liquid solid liquid catalyst (Tri phase catalyst) is of great industrial importance because of its reusability property. The effect of various parameters was studied on %conversion and the selectivity of DBS. So one can selectively produce benzyl mercaptan or di benzyl sulphide by selecting an appropriate process condition .Low sulphide concentration or higher value of MEA/H_2S ratio, high benzyl chloride concentration and long reaction time favours the formation of DBS. The reverse is for the formation of benzyl mercaptan.For higher conversion of

benzyl chloride, the concentration of benzyl chloride is kept low, MEA/H_2S ratio is also kept low. The conversion of benzyl chloride increases with increase in the catalyst loading upto 10%(w/v). After this concentration the there is not much notable change in the conversion value but the selectivity of DBS continue to increase with the increase in catalyst loading.

CHAPTER 5

SUMMARY AND CONCLUSION

CHAPTER 5

SUMMARY AND CONCLUSION

Abstract

This chapter summarizes the concluding remarks of previous chapter.

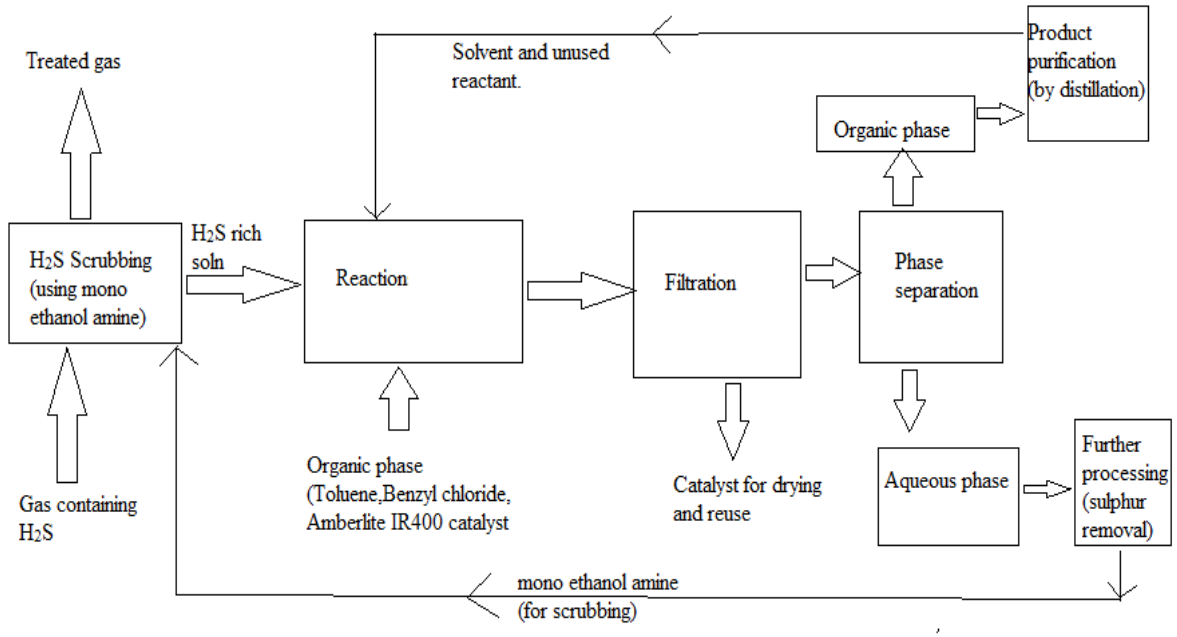
5.1 INTRODUCTION

The work done in this thesis has led to the development of an industrial process for generation of dibenzyl sulphide and benzyl mercaptan using hydrogen sulphide gas present in various byproduct gas streams. According to the present process, H_2S present in the gas stream can be used for the production of DBS and BM in two steps:

1) Removal of H_2S gas from the gas stream by absorbing it in monoethanol amine solution.

2) Second step involves the production of DBS and BM using the H_2S rich MEA obtained from the first step.

The present process is shown in the following scheme 5.1.



Scheme 5.1

5.2 SUMMARY AND CONCLUSION

The reaction of H_2S rich monoethanol amine and benzyl chloride present with toluene as solvent produced DBS and BM which is very much valuable. One can selectively prepare DBS by keeping the initial sulphide content high, long reaction time and high benzyl chloride conversion. In this process, the two active ion pairs QSQ and QSH moved from the aqueous phase to the organic phase where it forms DBS and BM. The maximum conversion of 90% and maximum selectivity of 46 % has been found. It needs further treatment as the complete utilization was not observed even after 6hours, so some sulphide must have remained inside the MEA solution. The selectivity is low, this may be due to the reason that reaction is occurring not occurring at high temperature. The amberlite IR400 has great reusability property and can be reused again. There is about 21.6% fall in catalytic activity even after 4 cycle of use. So this catalyst can be industrially very valuable for this process.

CHAPETR 6

SCOPE FOR FUTURE WORK

CHAPTER 6

SCOPE FOR FUTURE WORK

ABSTRACT

This chapter focuses on scope of further work based on results and conclusion of present study. This chapter is dedicated to finding the area where improvement can be done to get better conversion and selectivity.

6.1 INTRODUCTION

The work described in this thesis deals with the preparation of DBS and BM by using H_2S rich monoethanol amine and benzyl chloride by using triphase catalyst with solvent. There are number of things where we could have and should have tried but we could not do because of lack of facility, finance and delay in the supply of materials.

6.2 INVESTIGATION OF MECHANISTIC PATHWAY

The mechanistic pathway shown in chapter 4 is based on some earlier studies and data. Aqueous phase can also be analyzed to know the ions present in it and to know about mechanistic pathway of the triphasic system.

6.3 FINDING OUT EFFECT OF OTHER PARAMETERS

Effect of variation of temperature can be studied to know about the reaction kinetics as it is very necessary for the modeling of the process. This can help in increasing the conversion and decreasing the use of catalyst, reaction time.

The effect of pH can be studied as concentration of S^{2-} and HS^{-} has very important role to play in the selectivity. The concentrations of sulphide and hydrosulphide ion depend upon pH.

In present study, toluene has been used as a solvent and swelling was observed in the catalyst. The solvent plays an important role on PTC reaction, as it affects the transport properties of PTC and active catalyst species (QSH and QSQ) (Yang et al). Other types of solvent like chlorobenzene, n-heptane can be used.

6.4 USE OF OTHER AQUEOUS PHASE

The aqueous phase used in the present work is monoethanol amine which can absorb both CO_2 and H_2S. Our present work is applicable for the stream containing H_2S and CO_2, only if the aqueous phase is H_2S selective.

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